

Composition Studies on Tobacco. XV.

Steam-volatile, Neutral Substances in Smoke from Blended and Unblended Cigarettes

Purchased by

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The differences in the steam-volatile, neutral substances of cigarette tobacco types and grades have been recently described (Burdick *et al.*, 1963). In a continuation of this work, a survey of these substances in smoke condensates from blended and unblended cigarettes prepared from the above tobacco types has now been completed. Although a large number of publications exists on cigarette smoke composition, a general survey of this nature has not previously appeared, as far as we are aware.

Method

All cigarettes were manufactured on a commercial, production-line machine, were 85 mm in length, and contained no filters or additives. Six types of cigarettes were studied, four unblended (straight flue-cured, burley, Maryland and Turkish) and two blended. One blend (FBMT) consisted of 40% flue-cured, 35% burley, 5% Maryland, and 20% Turkish; the other blend (FBM) was 60% flue-cured, 35% burley, and 5% Maryland. The cigarettes were smoked on an automatic, constant-time smoking machine operating on a principle generally similar to that described by Mumpower *et al.* (1961). The automatic feature of the machine permitted a maximum of nine puffs per cigarette in a given cycle in which 15 cigarettes were smoked. The puff volume, puff duration, and puff rate were 35 ml, two

sec, and one puff per min, respectively. Smoke condensates were collected in spiral glass traps (Scheppartz, 1959) cooled in Dry Ice—acetone. The moisture content of the cigarettes was 12.1–13.6% except for the Maryland which was 14.1%. One hundred five cigarettes of each type were smoked and the steam-volatile neutrals obtained by the following method.

The traps were washed successively with portions of redistilled ether (150 ml total) and 5% aqueous sodium hydroxide (25 ml total) until the condensate was dissolved. The ether and alkaline washings were placed in the same container and sodium chloride was added until the aqueous layer was saturated. The layers were separated into an ether layer (A) and an aqueous layer. The aqueous layer was then extracted twice with ether (30 ml total), which resulted in a final aqueous extract (B) and an ether extract. This ether extract was pooled with A and the pooled extract was designated C. Bases and acids were removed from C by successive extraction with 12% hydrochloric acid solution (5 times, 165 ml total) and 5% aqueous sodium hydroxide solution (5 times, 180 ml total), which resulted in an ether solution of neutral substances (D), an acid solution of bases (E), and an alkaline solution of acids (F). E and F were each washed twice with 15 ml ether and all ether washings were added to D. F was pooled with B for future work on acidic substances. D (neutral substances) was washed with 5 ml portions of sodium chloride saturated water to remove traces of alkali, after which D was added to the pot of a steam

distillation system. The pot contents were steam distilled and both the ether and 1000 ml of distillate were collected in the cooled receiver. To the receiver was added sufficient sodium chloride to saturate the aqueous layer and the layers were separated into an ether solution (G) and an aqueous distillate. The distillate was then extracted twice with a total of 300 ml ether. The latter was pooled with G, and the pooled solution dried over sodium sulfate. The dried ether solution was concentrated to 0.5–0.6 ml (H) and the latter was investigated by gas chromatography. For each cigarette type an aliquot of concentrate (H), equivalent to 3 mg of residue (usually about 7–14 μ l) was injected. The methods for solvent removal, residue determination, and gas chromatographic separations were identical with those previously used (Burdick *et al.*, 1963).

For quantitative comparison, peak areas were obtained using a planimeter and appropriate baseline corrections. For each peak an "Equivalent Peak Area" (EPA), similar to that previously described, was calculated by EPA = $\frac{55 AC}{VP}$ in which A

was the measured peak area (cm^2), C was the volume (μ l) of the concentrate (H), V was the volume (μ l) of the injected aliquot, and P was the average length (%) of cigarette smoked for the particular cigarette type. Such EPA values represent a theoretical peak area which would be obtained on injection of the entire quantity of steam-volatile neutral substances in the condensate resulting from smoking 55% of each of 105 cigarettes of a given type.

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The selection of this basis for expressing the results is discussed below.

Results and Discussion

Pertinent properties of the six types of cigarettes are summarized in Table 1. The characteristic differences in filling power and burn rate of the unblended tobaccos are evident. The S values (ml mainstream smoke per g cigarette smoked) for burley and Maryland reflect the differences in burn rate and are lower than those for flue-cured or Turkish. The calculated S values for the blends (375 and 386 for FBM and FBMT, respectively) based on the known percentages of the tobacco types in the blends correlate well with the observed S values (Table 1) indicating that the individual tobaccos therein may be contributing to the overall burning characteristics in an additive manner rather than in a "synergistic" or "antagonistic" fashion.

Optimal gas chromatographic

Table 1. Physical data on test cigarettes.

Characteristic	Cigarette type					
	Flue-cured	Burley	Maryland	Turkish	FBM blend*	FBMT blend*
Avg wt cigarette (g)	1.37	.937	.844	1.52	1.17	1.19
Avg wt cigarette smoked (g)	.669	.573	.505	.672	.740	.721
Avg % cigarette smoked**	49	61	60	44	63	61
No. puffs	8	5	5	9	8	8
Avg butt length (mm)	.45	33	35	48	30	33
ML mainstream smoke per g cigarette smoked (S)***	419	305	346	469	378	388

*Blends of flue-cured, Burley, Maryland with or without Turkish. See Method for blend compositions.

** Based on initial weight of cigarette and weight of cigarette smoked.

*** See Results and Discussion.

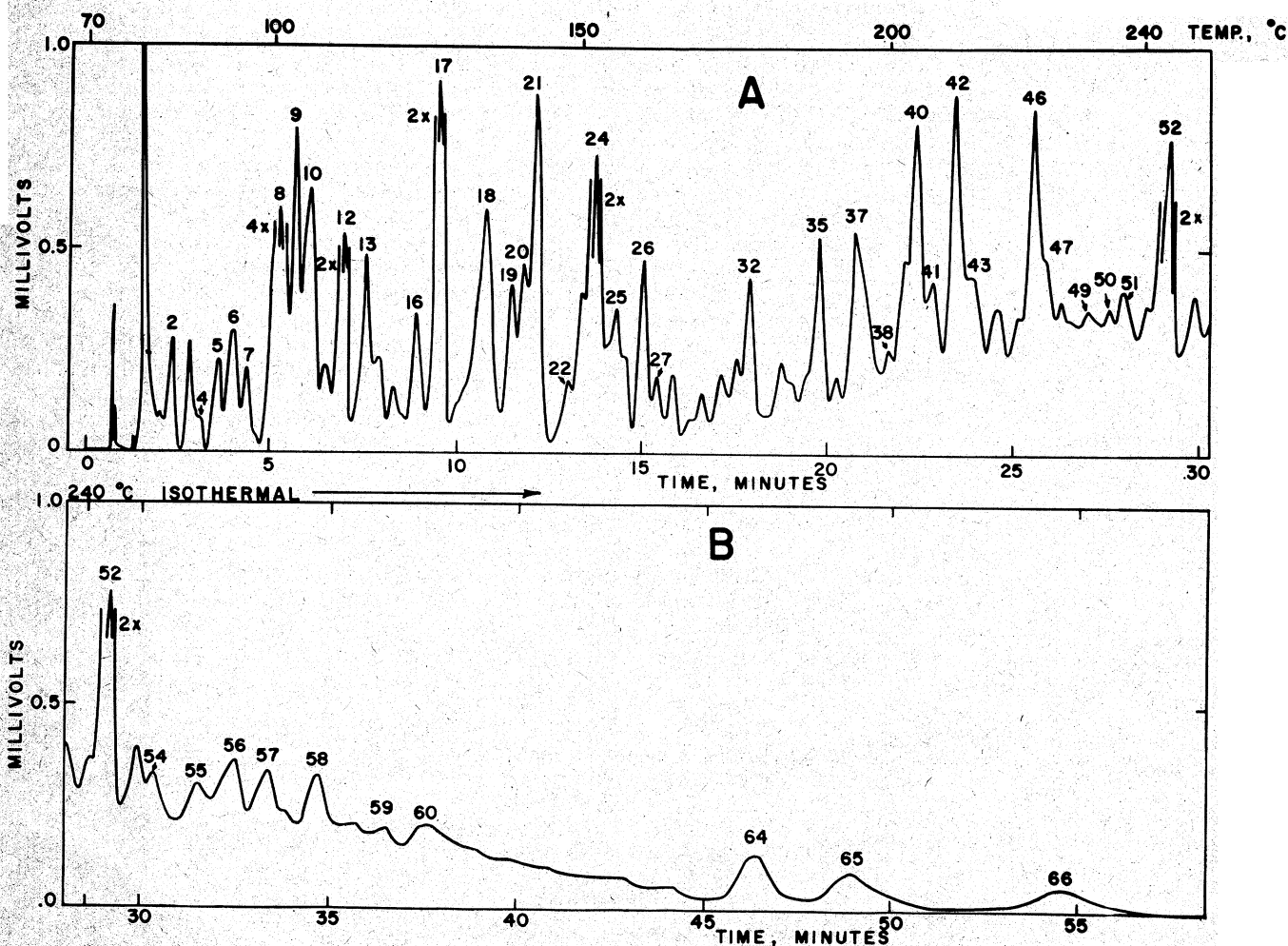


Figure 1. Chromatogram of steam-volatile, neutral substances of smoke condensate from Turkish cigarettes. Twenty percent Carbowax 20 M on acid-washed Chromosorb W (60-80 mesh), 10 ft. x 0.25 in. column, 75 ml helium per min, programmed 6° C per min from 70° to 240° C (A) followed by isothermal operation at 240° C (B).

Table 2. Quantitative differences in the major components of the steam-volatile neutral substances of various smoke condensates.

Peak No.	Ratios of equivalent peak areas (EPA) for indicated cigarette type*						EPA (cm ²) (Flue-cured)
	F	B	M	T	FMB	FMT	
5	1.0	0.48	0.52	0.69	0.45	0.45	178
6	1.0	1.77	1.41	2.31	1.44	2.97	109
7	1.0	1.06	1.44	1.69	1.39	1.47	89
8	1.0	1.53	1.06	4.26	1.47	2.59	337
9	1.0	1.57	3.91	1.48	1.87	2.44	188
10	1.0	1.17	1.79	1.29	1.27	1.47	337
12	1.0	0.54	0.58	1.32	0.73	0.65	525
13	1.0	0.55	0.52	0.78	0.54	0.63	307
16	1.0	0.91	0.66	0.84	0.75	0.74	198
17	1.0	0.71	0.58	1.07	0.68	0.68	1140
18	1.0	1.01	0.58	0.66	0.74	0.92	743
19	1.0	0.89	0.55	0.72	0.55	0.68	317
21	1.0	0.52	0.40	0.68	0.58	0.59	714
22	1.0	0.65	0.47	0.60	0.45	0.43	159
24	1.0	0.56	0.38	0.52	0.52	0.51	1377
25	1.0	0.73	0.54	0.76	0.65	0.55	386
26	1.0	0.58	0.53	0.76	0.46	0.42	248
32	1.0	1.17	0.78	1.27	0.59	0.67	168
35	1.0	0.23	0.24	0.30	0.14	0.14	832
37	1.0	0.68	0.59	0.69	0.69	0.51	624
40	1.0	0.12	0.11	0.47	0.27	0.20	813
41	1.0	0.25	0.26	0.43	0.23	0.42	297
42	1.0	0.34	0.24	0.62	0.38	0.26	763
43	1.0	0.29	0.39	0.58	0.41	0.42	258
46	1.0	0.54	0.78	0.61	0.46	0.53	624
47	1.0	0.38	0.26	0.37	0.26	0.33	218
51	1.0	0.13	0.24	0.37	0.15	0.22	159
52	1.0	0.45	0.30	0.34	0.55	0.40	2487
55	1.0	0.29	0.28	0.35	0.29	0.26	307
56	1.0	0.62	0.30	0.54	0.37	0.30	357
57	1.0	0.34	0.30	0.70	0.31	0.34	277
58	1.0	0.61	0.73	0.52	0.25	0.23	248
59	1.0	0.14	0.10	0.35	0.15	0.08	287
60	1.0	0.09	0.08	0.12	0.21	0.20	644
64	1.0	2.40	1.56	1.08	1.12	1.09	149
65	1.0	0.61	0.47	0.51	0.46	0.43	208
66	1.0	0.27	0.35	0.46	0.36	0.25	248
Total EPA area (cm ²)	17,300	9,810	8,580	12,000	9,370	9,600	17,300

*F = flue-cured, B = burley, M = Maryland, T = Turkish, FMB = blend without Turkish, FMT = blend with Turkish. See text for percentage composition of blends and definition of EPA.

separation of the neutral substances was obtained by programming a Carbowax² 20 M column as previously described. Figure 1 is a chromatogram of the condensate of the Turkish cigarettes. At least 66 peaks were evident. Comparison of this chromatogram was the previously published chromatogram of a similar fraction from Turkish tobacco leaves showed that, as expected, the smoke is more complex and has much more relatively volatile material which elutes at temperatures below 175° C. The chromatograms of the neutral sub-

stances from the other five cigarettes were qualitatively similar to the Turkish smoke but quantitatively different. Cochromatography of the neutral substances from all six cigarettes types in a single injection showed that all peaks chromatographed in an identical manner. These results parallel in a general way the previous findings on the steam-volatile neutral substances of cigarette tobaccos.

The quantitative evaluation of complex chromatograms requires many arbitrary decisions on such points as background corrections, measurements of inflections, and disposition of very small peaks. The quantitative evaluation presented herein should be accepted with the recognition of the necessity for

such subjectivity.

To compare the quantitative differences between the cigarettes, the 66 peaks were arbitrarily divided into "major" and "minor" peaks. A peak having an EPA of 150 cm² or more in at least one of the six types of cigarettes was considered a "major" one, and a peak of less than 150 cm² was "minor". As described above, the EPA values were arbitrarily based on the calculated amounts of the substances obtained on smoking 55% of each cigarette³ in a total batch of 105 cigarettes. Wide differences in burning rates and specific volumes as well as the design of the smoking machine made selection of this condition more desirable than the usual standards, such as amounts per g of tobacco smoke, per liter of smoke, or per cigarette smoked to an exact butt length.

All major peaks and certain minor ones of interest are labeled in Figure 1. Total EPA values, EPA values per peak for flue-cured cigarettes, and ratios of EPA values for the major peaks are shown in Table 2. The ratios of EPA values were arbitrarily based on the EPA values for flue-cured cigarettes. Peaks 2, 6, 8, and 10 contained some extraneous substances derived from the solvent (ether), but the bulk of the amounts in these peaks was obtained from the smoke. Values for total EPA are rounded off to three significant figures. For the four unblended cigarettes, the order of decreasing total EPA for the major peaks was flue-cured, Turkish, burley, and Maryland. Compared to the other three unblended cigarettes, flue-cured generally gave larger amounts of all peaks except for six peaks (6-10, 12) eluting below 110° C and two peaks eluting at higher temperatures (32, 64).

The blended cigarettes gave ratios of EPA values less than 1.0 except for peaks 6-10 and 64 (Table 2). To determine whether each tobacco in a blend contributed additively to the total EPA for the blend, a comparison of calculated and observed EPA ratios for the major peaks of the two blended cigarettes was made. For each peak, the percentage (expressed as a decimal) of a given tobacco in the blend was multiplied by the observed EPA ratio for the corresponding un-

² Use of a commercial product does not constitute endorsement by the U. S. Department of Agriculture over other products of a similar nature.

³ Fifty-five percent is approximately the mean of the six values for the average percentage of cigarette smoked (table 2).

blended cigarette (Table 2), and the resulting corrected ratios for the three (FBM) or four tobaccos (FBMT) in the blended cigarettes were added to give the "calculated EPA ratio". The differences between the calculated and observed EPA ratios are shown in Table 3. Except for peaks 6-10, the major peaks in both blends were smaller than expected, indicating that the patterns of combustion, pyrolysis, distillation, etc. of the individual tobaccos appear to be altered when the tobaccos are blended, at least with respect to the components in question⁴. Further work is required to establish this joint conclusively.

The quantitative differences in the minor peaks are shown in Table 4. Since the errors associated with these peaks (e.g. measuring areas, determining inflections, etc.) are much larger than those of the major peaks, a semiquantitative presentation is given in the table. The total EPA values for the minor peaks of all cigarettes follow in general the pattern for the major peaks. Only three peaks, numbers 4, 20, and 49, showed a majority of values greater than +1 (contain more than flue-cured cigarettes) among the six cigarette types. The tendency toward the blends showing less EPA than would be expected from an additive effect of constituent tobaccos may be present, although even a superficial appraisal on this point is difficult.

Limitations. Many of the limitations previously discussed in the report on leaf apply to the present work. However, fewer artifacts may be produced by the steam distillation of condensate by the above method than was the case with leaf. The preliminary separation of acidic and basic substances from the condensates before steam distillation of the neutral substances eliminates acid or base-catalyzed structural alterations and related changes on heating. The absence of significant amounts of heat-labile cellular constituents, i.e. proteins, sugars, etc., in smoke condensates eliminates a significant source of artifacts. However, the complexity of smoke condensates and the relatively drastic treatment of steam distillation make complete elimination of artifact formation difficult with this procedure.

Since the overall variability of the

Table 3. Percentage difference between calculated and observed ratios of Equivalent Peak Areas (EPA) for major peaks of blended cigarettes.

Peak No.	Percentage difference		Peak No.	Percentage difference	
	FBM ^a	FBMT		FBM	FBMT
5	-35	-39	37	-21	-37
6	+11	+91	40	-58	-62
7	+34	+25	41	-67	-29
8	+25	+41	42	-48	-60
9	+40	+69	43	-43	-34
10	+15	+27	46	-45	-29
12	-11	-26	47	-67	-46
13	-34	-19	51	-77	-58
16	-21	-20	52	-29	-38
17	-23	-24	55	-59	-55
18	-24	+1	56	-56	-60
19	-41	-23	57	-58	-50
21	-27	-20	58	-71	-69
22	-47	-44	59	-77	-85
24	-37	-29	60	-67	-56
25	-36	-34	64	-26	-29
26	-45	-46	65	-45	-67
32	-34	-39	66	-49	-58
35	-80	-75			

^aPercentage difference = $(100 \times \frac{\text{Observed ratio EPA}}{\text{Calculated ratio EPA}}) - 100$. Calculated ratios obtained from known percentage composition of blends (see Methods) and ratios reported for flue-cured, burley, Maryland, and Turkish cigarettes in Table 2. Observed ratios are given in table 2. See footnote table 2 for blend designations FBM and FBMT.

above method is not known, limits of statistical significance cannot be established. (However, one potential source of error, the variation of replicate injections of a concentrate, was investigated and found to be less than $\pm 5\%$ of the mean for duplicate injections.) Although the above data are presented quantitatively the findings have been evaluated in terms of trends rather than precise quantitative terms.

Identification. Peaks 35, 42, 43, 47, and 52 are similar to certain peaks previously described in tobacco leaf and tentatively identified as furfural, furfuryl alcohol, m-tolualdehyde, benzyl acetate, and neophytadiene, respectively. Only preliminary work has been done on the identification of the remainder of the peaks. Undoubtedly, many of the peaks, and especially those eluted at low temperatures, contain more than one substance since a large number of

low boiling, neutral compounds occur in smoke, many of which are difficult to resolve from complex mixtures.

Summary

A survey was made of the steam-volatile neutral substances in the smoke from blended and unblended cigarettes using a subjective method of evaluation, the assumptions of which are discussed in detail. In general, the gas chromatograms of four unblended (straight flue-cured, burley, Maryland, and Turkish) and two blended (flue-cured, burley, and Maryland with or without Turkish) cigarettes were qualitatively similar and quantitatively dissimilar. Of the steam-volatile neutral substances eluting in the gas chromatographic procedure, the decreasing order of total neutrals was flue-cured, Turkish, burley, and Maryland for the unblended cigarettes. Data are presented which show that the conden-

⁴This is in contrast to the above conclusions based on the calculated and observed S values which, however, reflect the overall burning properties.

Table 4. Relative amounts of the minor peaks of the steam-volatile neutral substances in various smoke condensates.

Peak No.	Relative amounts in indicated cigarette type*						EPA (cm ²) (flue-cured)
	PM	B	M	T	FBM	FBMT	
1	+1	-1	-4	-4	-2	-4	10
2	+1	-1	-4	-2	-3	+3	118
3	+1	-2	-1	-2	+2	-1	109
4	+1	+6	+6	+6	+6	+6	10
11	+1	-2	-2	-1	-3	-2	149
14	+1	-2	+2	-1	-2	+1	89
15	+1	-2	-2	-3	-3	-3	109
20	+1	+4	+2	+4	-1	-2	79
23	+1	-2	-2	+2	-3	-2	139
27	+1	-2	-3	-2	-3	-3	79
28	+1	-2	-3	+2	-2	-3	69
29	+1	+3	-1	+1	-1	-1	40
30	+1	-1	-2	-1	-3	-2	89
31	+1	-1	-2	-1	-2	-2	109
33	+1	-2	-2	-1	-3	-2	119
34	+1	-4	-3	-2	-3	-4	50
36	+1	-4	-3	-2	-3	-4	59
38	+1	+3	-1	-2	-2	-2	59
39	+1	-2	-3	-2	-3	-2	149
44	+1	-2	-3	-1	-2	-2	89
45	+1	-2	-2	+2	-2	+2	40
48	+1	-1	-3	-2	-3	-2	119
49	+1	+5	+3	+6	-4	+2	30
50	+1	-2	-2	-2	-3	-1	59
53	+1	-1	-3	-1	-3	-2	129
54	+1	-2	-3	-1	-2	-3	89
61	+1	-2	-3	-3	-2	-3	40
62	+1	-2	-4	-4	-3	-3	119
63	+1	-1	+1	+1	-1	-1	<10
Total EPA area (cm ²)	2,360	1,750	1,280	2,050	1,230	1,560	2,360

*Based on range of ratio of EPA: +6 = EPA ratio, >2.0; +5 = range of ratio, 1.75 - 2.0; +4 = 1.50 - 1.75; +3 = 1.25 - 1.50; +2 = 1.0 - 1.25; +1 = 1.0; -1 = 0.75 - 1.0; -2 = 0.50 - 0.75; -3 = 0.25 - 0.50; -4 = <0.25.

**See footnote, table 2, for designation of cigarettes.

sates from blended cigarettes have less of such neutral substances than would be expected if each tobacco in the blend contributed to the total neutrals in an additive fashion. More work is required to establish this point conclusively.

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